

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT : ROBERT J. TYNIK
SERIAL NO. : 10/822,057
CUSTOMER NO. : 23526
FILED : April 8, 2004
FOR : ORGANOAMMONIUM TUNGSTATE AND MOLYBDATE
COMPOUNDS, AND PROCESS FOR PREPARING
SUCH COMPOUNDS
ART UNIT : 1714
EXAMINER : James C. Goloboy

Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

SIR:

DECLARATION OF ROBERT J. TYNIK UNDER 37 C.F.R. §1.132

The undersigned, Robert J. Tynik, declares and says that:

1. I am the inventor of the invention described in the above-captioned application.
2. I am familiar with the Office Action in the above-captioned application mailed by the United States Patent and Trademark Office on December 11, 2006, and the prior art cited in that Office Action. I have reviewed the prior art references and rejections in the Office Action, in particular the rejection of claims 1-2, 4-10, 14-18 and 20-23 under 35 U.S.C. § 103(a) as

obvious over U.S. Patent No. 3,489,775 to de Roch *et al.* ("de Roch") in view of Freedman (*J. Am. Chem. Soc.*, 1959, 81, p. 3934-3839) ("Freedman"), claim 3 as being obvious over de Roch in view of Freedman and further in view of Krause (*J. Am. Chem. Soc.*, 1925, p. 1689-1694) ("Krause") and claims 11-13 and 24-29 under 35 U.S.C. § 103(a) as being obvious over de Roch in view of Freedman and further in view of U.S. Patent No. 4,626,367 to Kuwamoto *et al.* ("Kuwamoto") and U.S. Patent No. 5,562,201 to Papay *et al.* ("Papay").

3. The lubricating compositions in Kuwamoto are non-oil based water-soluble, metal-working lubricant compositions specifically designed to be used in water, not in oil. The molybdates and tungstates disclosed by Kuwamoto are corrosion inhibitors in aqueous systems. Paper Number 253 by the National Association of Corrosion Engineers (*Inhibitor Types*, Dean *et al.*) reported in Corrosion/81 is attached as Exhibit A to my declaration. This paper describes the mechanism of operation of the four major categories of corrosion inhibitors. In this paper, tungstates are included in the Barrier Layer Former category and are described as oxidizing inhibitors. The Barrier Layer Former category is discussed at pages 253/2 through 253/3 of the paper attached at Exhibit A. Tungstates operate by oxidizing any hydrogen ion (acid) to non-corrosive hydrogen by the following equation: $\text{WO}_4^{-2} + 4\text{H}^+ \rightarrow \text{WO}_2 + 2\text{H}_2 - 2\text{e}$. This therefore requires the formation of the tungstate anion (WO_4^{-2}) which can only form by the dissociation of a water-soluble tungstate in a very polar liquid

(water) by the following equation: $\text{Na}_2\text{WO}_4 \rightarrow 2\text{Na}^+ + \text{WO}_4^{2-}$. This dissociation can not occur in non-polar liquids like petroleum-based oils because the ions must be solvated by the polar liquid to form. Thus, the typical water-soluble tungstates, such as sodium tungstate, will not dissolve in petroleum-based oils and, therefore, will not dissociate into the required tungstate anions. Hence, one skilled in the art would not apply a water-soluble tungstate, and also would not apply a water-soluble molybdate, in an oil based system with any expectation of achieving corrosion inhibition or any other desirable property, such as anti-wear properties. The organoammonium tungstates and molybdates of the present invention are not water-soluble and, therefore, can not dissociate into tungstate or molybdate anions in water. In addition, when the organoammonium tungstates or molybdates are dissolved or dispersed in non-polar petroleum-based oils, they still do not dissociate into tungstate or molybdate ions.

4. It was discovered with the present invention that the organoammonium salts of the present invention exhibit anti-wear properties, particularly in the lubricating composition in amounts within the range of 0.025% to 5.0%, by weight. To demonstrate this, an oil-soluble molybdate and tungstate prepared in accordance with the present invention were compared to sodium tungstate in a modified 210 minute Falex Pin & Vee Block test applying a procedure similar to that described in the examples of U.S. Patent No. 6,369,005, for example the procedure described at

column 5, line 65 to column 6, line 11. Organoammonium tungstate and organoammonium molybdate were prepared by reacting $\text{WO}_4\text{H}_2\cdot\text{H}_2\text{O}$ or $\text{MoO}_4\text{H}_2\cdot\text{H}_2\text{O}$ with a di-tridecylamine product available from BASF, Madison, New Jersey which upon information and belief based on data from the manufacturer comprises predominately C_{13} amines, but also contains lesser amounts of C_{10} , C_{11} , C_{12} and C_{14} species.

5. The tested compositions comprising the organoammonium tungstate and organoammonium molybdate prepared with the materials discussed above and results are provided in the table attached as Exhibit B to my declaration. In columns A, B and C, an organoammonium tungstate, organoammonium molybdate and a mixture of the two were tested in Uninap 100SD oil at 700 ppm of metal. All three samples passed the full 210-minute test with the mixture (SGW-558-054) showing an apparent synergy with a very low mass loss of only 5.4 mg., a final temperature of 99°C , teeth wear of 149, wear of 0.010 inches and average coefficient of friction of 0.203. In columns D, E and F, aqueous solutions of sodium tungstate containing 350, 700 and 1400 ppm of tungsten were tested. These samples either failed immediately or after only 6.5 minutes, showing no anti-wear activity. In addition, in sample H, organoammonium tungstate (without oil) was dispersed in water using 1.0% of Triton X-100 surfactant to give 700 ppm of tungsten. The test was performed for 35 minutes and as indicated in the table of Exhibit B showed a very high rate of wear. Controls of pure water (Sample G) and water containing 1.0%


surfactant (Sample I) were also tested. As indicated in the table of Exhibit B, the pure water failed immediately and the surfactant sample was tested for 35 minutes and showed a very low rate of wear. Thus, indicating that organoammonium tungstate, like sodium tungstate, provides no lubricating/anti-wear properties in water. The sample in column J was prepared by adding an aqueous solution of sodium tungstate to Uninap oil and then stripping off the water leaving finely-divided solid sodium tungstate in the oil. This sample, containing 700 ppm of tungsten, failed almost immediately. This data demonstrates the lack of any anti-wear activity by the typical, water-soluble corrosion inhibitor sodium tungstate. It is expected that water-soluble molybdates also would not demonstrate any anti-wear activity.

6. In the Office Action the examiner states: "Therefore the use of molybdates and tungstates of de Roch as corrosion inhibitors in a lubricating composition in the amounts taught by Papay meet the conditions of de Roch in a lubricating composition, as Kuwamoto teaches that they are effective corrosion inhibitors." (Office Action pp. 7-8) The molybdates and tungstates of de Roch were neither designed nor intended for use in lubricating compositions and, therefore, lack the necessary solubility in petroleum-based lubricating compositions. None of the particularly preferred molybdates and tungstates of de Roch were made from organic nitrogenous bases having sufficient lipophilicity to impart oil solubility to the molybdates and tungstates. In order for molybdates and tungstates to

be effective anti-wear agents in petroleum-based lubricating compositions, they must have sufficient solubility in the oil or lubricating composition. If these molybdates and tungstates do not have sufficient solubility in lubricating compositions, then it will not be possible to incorporate a sufficient amount of the molybdates and tungstates to achieve the desired level of anti-wear activity. To demonstrate the importance of solubility on anti-wear performance, dihexylammonium tungstate was prepared from dihexylamine, one of the more lipophilic of the preferred embodiments of the organic nitrogenous bases in accordance with the teachings of de Roch. The dihexylammonium tungstate was combined with the Uninap 100 SD Oil and the composition and test results for the Falex Pin & Vee Block test are set forth in the table attached as Exhibit B to my declaration (Sample K). The dihexylammonium tungstate of de Roch was found to be nearly insoluble when added at only 0.14 weight percent (700 ppm of W) to the base oil used for the Falex Pin & Vee Block test. All un-dissolved material was dispersed in the oil and the sample was tested. As can be seen in the column for sample K, this sample failed in less than two minutes. Moreover, comparison of the compositions of C₁₃ tungstates and molybdates formulated from the BASF di-tridecylamine product in accordance with the present invention for samples A, B and C which passed the Falex Pin & Vee Block test with the results from the de Roch C₆ composition for sample K shows that the de Roch compositions, and in general the shorter chained dialkyl amines, will not achieve a tungstate or

molybdate composition that will provide effective properties, such as wear resistance, in the oil-based lubricating compositions of the present invention.

7. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


Robert J. Tynik

March 12, 2007

NORRIS, McLAUGHLIN & MARCUS
P.O. Box 1018
Somerville, NJ 08876-1018
(908) 722-0700

101221-680

CORROSION/81

The International Corrosion Forum Sponsored By the National Association of Corrosion Engineers / April 6-10, 1981 / Sheraton Centre, Toronto, Ontario, Canada.

INHIBITOR TYPES

Sheldon W. Dean, Jr.
Air Products & Chemicals, Inc.
P. O. Box 538
Allentown, PA 18105

Richard Derby
Air Products & Chemicals, Inc.
P. O. Box 427
Marcus Hook, PA 19061

Glenn T. von dem Bussche
Air Products & Chemicals, Inc.
P. O. Box 538
Allentown, PA 18105

ABSTRACT

Four major categories of corrosion inhibitors have been identified based on the mechanism of operation, including barrier layer formers, neutralizers, scavengers, and miscellaneous types. The barrier formers have been further classified into oxidizers, adsorbed layer formers, and conversion layer formers. The barrier layer formers are generally effective in reducing both the cathodic and anodic reaction rates except for the oxidizing inhibitors which rely upon driving the metal potential in the positive (oxidizing) direction to take advantage of a passive layer which is stable at higher potentials. The neutralizing inhibitors reduce the corrosivity of the environment by removing hydrogen ions from the environment, thereby reducing the concentration of cathodic reactant. Some scavengers operate on a similar principle. Materials such as hydrazine and sodium sulfite are added to boiler systems to remove trace quantities of oxygen which is also a cathodic reactant. There are also a number of scavenging inhibitors added to products such as lubricants, chlorinated hydrocarbons, etc., which operate by removing free radicals and other active species which can ultimately become acidic or corrosive. Miscellaneous inhibitors include materials such as scale inhibitors and biological growth inhibitors which prevent corrosion by interfering with other processes. In selecting inhibitors, it is important to consider the mechanism of the corrosion process which must be inhibited.

Publication Right

Copyright by the author(s) where copyright is applicable. Reproduced by the National Association of Corrosion Engineers with permission of the author(s). NACE has been given first rights of publication of this manuscript. Requests for permission to publish this manuscript in any form, in part or in whole, must be made in writing to NACE, Publications Dept., P.O. Box 218340, Houston, Texas 77218. The manuscript has not yet been reviewed by NACE, and accordingly, the material presented and the views expressed are solely those of the author(s) and are not necessarily endorsed by the Association.

Printed in USA

The discovery that certain chemical substances, when present in low concentrations in aqueous systems, would prevent the corrosion of structural and engineering materials exposed to these solutions has led to the development of a technology concerning corrosion inhibitors. There are many systems in which the use of corrosion inhibitors is the simplest and most economical approach to controlling corrosion. Corrosion inhibitors have thus taken their place beside corrosion resistant alloys, barrier coatings, electrochemical protection systems, and other techniques as primary weapons in the fight against corrosion. There are, however, a substantial number of different types of corrosion inhibitors which are used in various applications. In selecting corrosion inhibitors for a specific corrosion problem, the formulator should have some understanding of the mechanism of the corrosion process as well as some qualitative concept as to how corrosion inhibitors might function in this particular application.

There are a surprisingly large number of different corrosion inhibitors which are used in various applications and they function in a variety of ways. In some cases the mechanism of inhibition is poorly understood. However, in most cases we have at least a qualitative understanding of how the inhibitor functions.

The purpose of this paper is to provide a broad overview of the different types of corrosion inhibitors used commercially. Because of the large number of materials which are used as corrosion inhibitors it has been necessary to develop a classification system. We have attempted to classify these materials by the mechanism of their inhibitive action. This approach has a problem when it comes to materials which function by mechanisms we do not understand. However, these materials are relatively few and should not cause serious problems. This paper presents a classification system for corrosion inhibitors and provides examples for each classification of inhibitor, but it is not intended to be a comprehensive list of corrosion inhibitors.

Four general categories of corrosion inhibitors have been identified: barrier layer formers, neutralizers, scavengers, and miscellaneous. These categories are discussed below.

BARRIER LAYER FORMERS

Corrosion inhibitors, which form barrier layers on the corroding metal surface, form the largest category of corrosion inhibitors. These materials have the ability to deposit on the metal surface and interfere with the corrosion reaction and thereby lower its rate to an acceptable value. This type of inhibitor has received the most attention from the technical community and is generally thought of when corrosion inhibitors are mentioned. There are a number of different types of corrosion inhibitors within this category and these will be discussed below.

Adsorbed Layer Formers

The corrosion reaction can be inhibited by materials which adsorb strongly to the metal surface and interfere with either the cathodic and/or anodic reactions occurring at the adsorption site. If the adsorption process is relatively complete and the surface coverage is total, then the corrosion

reaction can be reduced by many orders of magnitude. Materials such as the acetylenic alcohols have been shown to function in this way on steel in hydrochloric acid.[1] Other organic nitrogen compounds, such as quinoline, some of the aromatic amines and some quaternary salts are also very effective in strong acid solutions.[2, 3] Organic sulfur compounds, such as thiourea are also effective as are other organic compounds containing group 5A or 6A periodic chart elements. Inorganic compounds, such as sulfides, arsenic, antimony, and halides also function as adsorbed layer inhibitors in strong acid solutions.

Most strong acid inhibitors interfere with one or more of the rate-limiting steps in the dissolution process. Usually the most effective inhibitors interfere with both the anodic reaction and the cathodic reaction so that there is not a marked shift in corrosion potential accompanying the process. Strong acid inhibition is important in a number of areas including oil well acidizing, metal pickling, and acid cleaning. Table I provides a more detailed compilation of strong acid inhibitors.

In neutral pH solutions adsorbed layer inhibitors are also available, although their use is not as widespread. Under these conditions the primary cathodic reaction is usually the reduction of dissolved oxygen rather than reduction of hydrogen ions, as in the case of strong acids. The potential driving force for this reduction of dissolved oxygen reaction is so much greater than that for the reduction of hydrogen ions that inhibition through simple adsorption is more difficult. Again, nitrogen-containing organics, such as benzotriazole and related compounds are very effective for copper alloys and to a limited extent for steel. Other nitrogen, sulfur and oxygen-containing organics, such as sodium benzoate and sodium mercaptobenzothiazole are also effective. There are a few inorganic cations such as zinc and to a lesser extent cadmium which are effective as cathodic inhibitors in neutral and slightly acid solutions.[4] Examples of adsorbed layer inhibitors for neutral solutions are given in Table II.

The effectiveness of these adsorbed layer inhibitors is usually evaluated in terms of how much they reduce the overall corrosion reaction. The reduction of the corrosion reaction is expressed as % inhibition with 100% being total inhibition and 0%, no inhibition. The percent inhibition is calculated according to the relationship:

$$\% \text{ inhibition} = 100 \left(\frac{R - R^*}{R} \right) \quad (1)$$

where R = corrosion rate without inhibitor

R^* = corrosion rate with inhibitor

These inhibitors are also classified according to how they affect the component electrochemical reactions which make up the overall corrosion process. Figures 1-3 show electrochemical polarization diagrams for cathodic, anodic, and mixed inhibitors. In general, if the inhibition process is accompanied by a shift in the corrosion potential in the negative direction, then the inhibitor is a cathodic inhibitor. If the shift in potential is in the positive direction, then the inhibitor is an anodic inhibitor. If there is no or very little shift, both reactions are being inhibited, then the inhibitor is a mixed inhibitor.

Oxidizing Inhibitors - Passivators

Passivators are another important type of barrier layer former. They are useful in aqueous solutions within the neutral range. These inhibitors function by shifting the electrochemical potential of the corroding metal into a region where a stable, insoluble oxide or hydroxide forms which protects the metal surface. This type of inhibitor is especially effective on steels, although it is also effective on copper base alloys and certain other alloy systems. Chromates and nitrites have been found to be very effective for inhibiting steel in neutral environments.

The major advantages of this type of inhibitor are that it is relatively inexpensive, effective at low concentrations, and it reduces the corrosion rate of steel to very low values, i.e., less than 4 $\mu\text{m/y}$. Figure 4 shows a polarization diagram typical of steel in an aqueous system showing the anodic polarization curve with the development of passivity. The use of an oxidizing inhibitor such as sodium nitrite shifts the cathodic polarization curve in the positive direction, thus stabilizing the corrosion potential in the passive region. With the environmental problems caused by chromates, these materials have become relatively unavailable as corrosion inhibitors. As with nitrites, the problems of nitrosamine formation coupled with pollution control considerations have also made these inhibitors less popular. Consequently, there has been renewed interest in other types of oxidizing inhibitors such as molybdates and tungstates. These materials are not as strongly oxidizing and are of substantially higher cost. Table III shows a compilation of the electrochemical reduction potential of various potential passivating type inhibitors.

Conversion Layer Formers

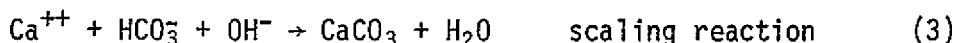
The passivating inhibitors rely on the development of an insoluble metal oxide or hydroxide which forms in situ on the metal surface. This layer forms the barrier to the corrosion process. Another approach which can be used is the addition of materials to the environment which form insoluble compounds on the metal surface without relying on the oxidation requirement of the passivating inhibitors.

Phosphates are probably the most widely used type of material in this category. They are used extensively in cooling water inhibitors. The principle of operation is that they form an insoluble iron phosphate on the metal surface and this layer builds up to sufficient thickness to provide an apparent passivity. Because ferrous phosphate does have some solubility in water, the corrosion reaction is not totally eliminated but rather reduced to a manageable degree.

Silicates are also used in some applications, especially for aluminum alloys. Ferrous sulfate has been used to inhibit copper alloys in once-through heat exchangers using natural waters as the cooling medium. In this case, the ferrous sulfate reacts with oxygen at the copper alloy surface to form a film of FeOOH which in turn provides improved resistance to erosion/corrosion.[5] Other examples of conversion layer inhibitors are given in Table IV.

It should be noted that the conversion layer type inhibitors are aided frequently by the presence of divalent cations, such as zinc, calcium, and magnesium. These cations tend to suppress the solubility of the iron compounds as well as interfering with the cathodic reduction of oxygen at the metal surface.

In neutral solutions the presence of calcium and magnesium ions also inhibit corrosion by the formation of an insoluble calcarious scale on the metal surface. The controlling reactions are:



The buildup of calcarious scale effectively blocks diffusion of oxygen to the cathode areas and gradually reduces the corrosion rate. This mechanism occurs frequently in hard well waters and in sea water and as a result, other inhibitors are sometimes not required.

In general, the conversion layer type inhibitors are less effective and more prone to control problems than the passivating inhibitors, but they have become very attractive because of their non-toxic characteristics.

NEUTRALIZING INHIBITORS

In many systems the corrosion process is driven by the reduction of hydrogen ions to hydrogen gas.



In neutral water at ambient temperatures the concentration of hydrogen ions is relatively low, especially as compared to the concentration of dissolved oxygen so that this reaction is not usually considered significant. However, at higher temperatures the diffusivity of the hydrogen ion increases and frequently its concentration as well, so this can become a significant factor. However, even at ambient conditions, chemical processes can occur locally which liberate hydrogen ions and these can contribute to the corrosion process.[6] As a result, a class of inhibitors has been developed whose primary function is to reduce the hydrogen ion concentration in the environment. A list of different types of neutralizing inhibitors is given in Table V.

This approach has been especially useful in treatment of boiler waters. In this case, weak acids such as carbonic acids, which are not normally a problem at ambient temperatures, become extremely corrosive. As a result, materials such as morpholine, cyclohexylamine, and ammonia are added to boiler waters in order to suppress the free hydrogen ion concentration. These materials are valuable because they react with the hydrogen ion in the boiler water according to a reaction similar to one shown below:



They are also weak bases, and consequently they do not form high concentrations of hydroxyl ions which can be very corrosive and subject steel to caustic cracking. In addition, these materials are volatile and can be carried into the steam to prevent carbonic acid attack in the condensate.

Neutralizing inhibitors are also used in oil field applications. Crude petroleum produced from the ground frequently contains a brine which contains hydrogen sulfide. This brine is extremely corrosive to carbon steel as it is produced. Above ground disposal of this brine is usually not possible because of environmental restrictions. In addition, its reinjection into the producing reservoir serves to stimulate further production. In order to control the corrosion which accompanies handling this material, it has been found that amines are effective. These materials react with the hydrogen sulfide to remove the hydrogen ion content as well as acting as an adsorbed layer inhibitor, as discussed above.

Basic materials such as sodium carbonate (soda ash), ammonia, and sodium hydroxide are commonly used in both the chemical process industries and the petroleum refining industries to control corrosion caused by small quantities of acidic material such as hydrogen chloride, carboxylic acids, carbon dioxide, and acidic phenols and related compounds. These acidic materials are present in small quantities in many process streams. However, because of separation processes such as distillation, these acidic materials can concentrate in specific areas and cause severe corrosion. The addition of basic materials such as soda ash and ammonia, etc., tends to remove the hydrogen ions which cause the corrosion process as well as changing the relative volatility of the acidic materials and thereby preventing localized accumulation within the separation unit.

Washing with a dilute soda ash solution is also used to remove sulfur compounds in petroleum refinery equipment during shutdowns.[10] These sulfur compounds would otherwise react with oxygen and form polythionic acid, which leads to very rapid intergranular cracking of sensitized stainless equipment.

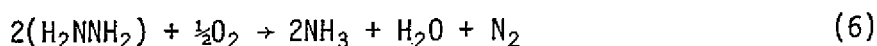
Neutralizing inhibitors are also used in ethylene glycol cooling systems to prevent the development of acidic conditions within such systems. Ethylene glycol can be oxidized to oxalic acid which is extremely corrosive to many alloys. The use of buffers such as sodium borate, sodium phosphate, and to a lesser extent, sodium silicate, can delay the onset of corrosion from this oxalic acid by reacting with the hydrogen ions and acting as a buffer.

SCAVENGERS

The neutralizing inhibitors described above are added to remove or react with hydrogen ions. However, in many systems there are other corrosive materials present in small quantities or concentrations which can cause equally severe problems. Inhibitors which remove such chemicals must be tailored for the particular corrosion process which is occurring in the system of interest.

Perhaps the most widely used scavenger system is employed in boilers to remove oxygen from the feedwater. Typical techniques such as steam stripping can remove the bulk of dissolved oxygen from water, however such methods become increasingly costly when the last traces of oxygen must be removed from

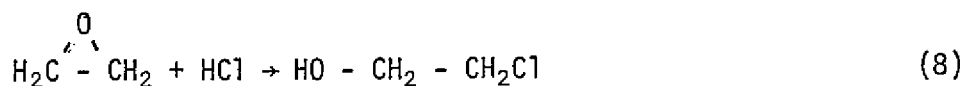
the boiler feedwater. In these cases, chemical techniques for oxygen removal become much more attractive. Perhaps the two most widely used scavengers in boiler systems are hydrazine and sodium sulfite. Chemical reactions which occur in both of these cases are shown below:



The hydrazine process is clearly a cleaner reaction in the sense that the reaction products are volatile and useful in terms of controlling pH, however hydrazine is more expensive than sulfite and therefore its use is generally restricted to high pressure boiler applications. Both sulfite and hydrazine require the addition of catalysts to the system in order to make these chemicals effective within the framework of residence times within most commercial boilers. As a result, proprietary formulations employing both neutralizing inhibitors and oxygen scavengers are generally used to treat boiler waters.

Another class of scavenging inhibitors is used to handle organic compounds which tend to break down to form acidic decomposition products. Chlorinated hydrocarbons such as 1-1-1 trichloro-ethane have been widely used as cleaning solvents in both the dry cleaning and metal finishing industries. These materials can decompose in the presence of water and higher temperatures to form hydrochloric acid, HCl, in small quantities, which is of course very corrosive to steel, aluminum, and other structural materials. This problem is handled by adding small concentrations of inhibitors which either react with any hydrogen chloride or which interfere with the decomposition process. Volatile amines have been used to react with the hydrochloric acid and chemicals such as dioxane and methyl butynol have also been found to be effective in preventing the decomposition process from occurring.

Another approach which has been used to scavenge small concentrations of hydrochloric acid in non-aqueous systems has been to add ethylene oxide. This chemical reacts with hydrochloric acid according to the following reaction:



The ethylene chlorohydrin resulting from this reaction is relatively non-volatile and is usually separated from the process. A variety of other scavengers are frequently used in petroleum products such as high performance lubricating oils, greases, and related compounds. Materials such as hydroquinone are effective in blocking the peroxide-free radical mechanism which, if left uninhibited, would result in the formation of carboxylic acids which are corrosive.

MISCELLANEOUS

There are a variety of other inhibitors which have been developed to interfere with processes which result ultimately in corrosion. In many cases, processes involved also lead to other undesirable consequences so that the inhibitors are not just corrosion inhibitors but have other desirable benefits as well. An example of this is the biocides which are used in cooling water applications. There are a variety of bacteria that can grow in aqueous systems which also promote localized corrosion of steel and other materials of construction. The sulfate-reducing bacteria are probably the most widely known of these bacteria, but there are many others as well. The use of biocides such as quaternary ammonium compounds [8] can control both the corrosion and the fouling which result from excessive biological growth.

Another type of inhibitor which is used in cooling water systems is the scale inhibitors.[8] These are materials which are added to the system to prevent growth of deposits on heat transfer surfaces due to precipitation of insoluble species such as calcium carbonate. These materials function by interfering with the normal crystal growth and thereby form soft, non-adherent precipitates in solution rather than on the metal surface.

The prevention of deposits on the metal surfaces minimizes problems from deposit corrosion or pitting corrosion. This type of corrosion is a form of crevice corrosion which can result in pitting and perforation. Deposits can also cause localized overheating resulting in corrosion. Materials which are used for this purpose are typically phosphonates, gluconates, and polyacrylic acids.

Chelating agents such as EDTA (ethylene diamine tetra-acetic acid) are also used for preventing scale formation. It should be noted, however, that chelating agents can increase the corrosion rate of many alloys by increasing the solubility of the protective corrosion products. These materials are also generally more expensive to use than the crystal growth modifiers.

There is a final group of corrosion inhibitors whose detailed mechanism is not well understood at this time. However, they are used in specific applications and are very effective. For example, water is added to commercial liquid ammonia to inhibit the stress corrosion cracking of carbon steel containment vessels.[9]

It has been found that 0.2% water addition to liquid ammonia practically eliminates the risk of stress corrosion cracking in structural steels. The function of the water in this case is not well understood, however it appears to act as a passivating inhibitor and encourages the formation of a more protective corrosion product on the steel. Similarly, it has been found that anhydrous ethylene glycol is corrosive to aluminum under certain conditions; the addition of a small quantity of water, e.g., 1%, inhibits the corrosion. In this case, the water seems to interfere with the tendency of aluminum to react directly with ethylene glycol to form a somewhat soluble Grignard type compound. The water may also encourage development of a more protective corrosion product film on the aluminum.

DISCUSSION

Corrosion inhibitors seem to fall into two general categories: first, those which act on the metal surface to improve its corrosion resistance; secondly, those which act in the solution to remove small concentrations of very corrosive constituents. Both approaches are used in specific applications and seem to be effective. Tailoring of a corrosion inhibitor to combat a specific corrosion problem usually requires a detailed knowledge of the corrosion process and some creative thinking on the part of corrosion engineers and scientists to develop a cost effective solution. In general, use of neutralizing and scavenging type inhibitors seems to be best suited to closed systems where such chemicals are not lost in the systems. In open systems where the process equipment sees large thruputs on a once-through basis, it is much harder to justify the use of inhibitors and any inhibitor selected for such an application must be effective at low concentrations and inexpensive.

The classification system proposed in this paper for inhibitors is summarized in Table VI. The classification of inhibitor types by function appears to give a fairly simple and concise approach, although it has limitations in cases where the mechanism is not known. Other people have classified inhibitors as organic versus inorganic, solution versus vapor phase, anodic versus cathodic. These classification systems certainly do not cover the full range of inhibitors which are currently in use and as such would not be suitable for a comprehensive and systematic approach to the classification of inhibitors. It would be desirable for NACE Unit Committee T3A to consider a systematic classification approach for corrosion inhibitors based on the approach used in this paper.

CONCLUSIONS

1. Corrosion inhibitors may be categorized as either barrier layer formers, neutralizing inhibitors, scavengers, or miscellaneous.
2. The barrier layer formers form the largest class of corrosion inhibitors and include the adsorbed layer inhibitors, oxidizing inhibitors, conversion layer formers.
3. The neutralizing and scavenger type inhibitors operate on the environment rather than on the metal surface and act by removing the corrosive species from the environment. As such, they represent a different approach to the problem of corrosion inhibition.
4. Based on the results of this survey it is recommended that a classification system be considered by NACE Unit Committee T3A on corrosion inhibitors.

References

1. S. W. Dean, H. J. Deitzer, and C. A. Cooper, Strong Acid Inhibition with Acetylenic Alcohols, Corrosion 79, Paper, No. 68, NACE, Houston, 1979.
2. M. G. Fontana and N. D. Greene - Corrosion Engineering, pp. 198-202, McGraw Hill, New York, 1967.
3. E. McCafferty, Mechanism of Corrosion Control by Inhibiting, H. Leidheiser, Jr., Ed. Corrosion Control by Coatings, p. 279 et. seq. Science Princeton, 1979.
4. H. H. Uhlig, Corrosion and Corrosion Control, Second Edition, pp. 257-291, John Wiley, New York, 1971.
5. F. L. LaQue, "Behavior of Metals and Alloys in Sea Water," in H. H. Uhlig, Ed., The Corrosion Handbook, p. 401, John Wiley, New York, 1948.
6. I. L. Rosenfeld, Crevice Corrosion of Metals and Alloys, in B. F. Brown et. al., Editors, Localized Corrosion, p. 378, NACE, Houston, 1974.
7. NACE Recommended Practice RP-01-70, Protection of Austenitic Stainless Steels in Refineries Against Stress Corrosion Cracking by Use of Neutralizing Solutions During Shutdown, NACE, Houston, 1970.
8. Cooling Water Treatment Manual, TPC Publication No. 1, pp. 8-11, NACE, Houston, 1971.
9. A. W. Loginow and E. H. Phelps, "Stress Corrosion Cracking of Steels in Agricultural Ammonia," Corrosion 18, pp. 299t-309t (1962).
10. R. H. Hausler in G. R. Brubaker and P. B. P. Phipps, Editors, Corrosion Chemistry, p. 262, ACS Symposium Series 89, Washington, D.C., 1979.
11. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, pp. 256-289, 493, et. seq., Pergamon Press, London, 1966.

TABLE I

Corrosion Inhibitors for Steel in Strong Acids


<u>Class</u>	<u>Compound</u>	<u>Formula</u>	<u>Range</u>	<u>Ref</u>
Acetylenic Alcohol	Propargyl	$\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}$		1
	Hexynol	$\text{HC}\equiv\text{C}-\text{CHOHC}_3\text{H}_7$		1
	Ethyl Octynol	$\text{HC}\equiv\text{C}-\text{CHOH}-\text{C}_7\text{H}_{15}$		1
Heterocyclic Amine	Quinoline	$\text{C}_6\text{H}_4\text{N}=\text{CHCH}=\text{CH}$ 		10
Fatty Amine	Rosin Amine			2
Sulfur Compound	Thiourea	$(\text{NH}_2)_2 \text{CS}$		2
	Sulfonated Oil	$\text{R}-\text{SO}_2\text{OH}$		10
Arsenic Compound	Arsenic Trioxide	AsO_3		2

TABLE II
Adsorbed Layer Forming Inhibitors for Non-Acid Systems

<u>Metal</u>	<u>Active Atom</u>	<u>Example of Inhibitor</u>
Copper Alloys	Nitrogen	Benzotriazole
		Tolytriazole
		Sodium Mercaptobenzothiazole
	Sulfur	Hexadecylmercaptan
Steel	Nitrogen	Sodium Mercaptobenzothiazole
		Imidazoline
		Fatty Amines

TABLE III
Electrochemical Potential of Some Oxidizing Inhibitors

<u>Type of Inhibitor</u>	<u>Reaction</u>	<u>E° vs. SHE</u>
Chromate	$10\text{H}^+ + 2\text{CrO}_4^{=}\rightarrow \text{Cr}_2\text{O}_3 - 6\text{e}$	1.3 - .0985 pH
Nitrite	$2\text{NO}_2^- + 8\text{H}^+ \rightarrow \text{N}_2 + 4\text{H}_2\text{O} - 6\text{e}$	1.52 - .079 pH
Nitrate	$2\text{NO}_3^- + 12\text{H}^+ \rightarrow \text{N}_2 + 6\text{H}_2\text{O} - 10\text{e}$	1.25 - .071 pH
Molybdate	$\text{MoO}_4^{=}\text{ + }4\text{H}^+ \rightarrow \text{MoO}_2 + 2\text{H}_2\text{O} - 2\text{e}$.606 - .118 pH
Tungstate	$\text{WO}_4^{=}\text{ + }4\text{H}^+ \rightarrow \text{WO}_2 + 2\text{H}_2 - 2\text{e}$.386 - .1182 pH
Pertechnate	$\text{TcO}_4^- + 2\text{H}_2\text{O}^+ \rightarrow \text{TcO}_2 + 4\text{H}^+ - 3\text{e}$.738 - .019 pH

Reference: Pourbaix (11)

TABLE IV
Conversion Layer Formers

<u>Metal</u>	<u>Class</u>	<u>Example</u>	<u>Layer</u>
Steel	Phosphate	Na_3PO_4	FeHPO_4
	Silicate	Na_2SiO_3	FeSiO_3
	Zinc Phosphate	ZnHPO_4	$(\text{ZnFe})\text{HPO}_4$
	Chromate	Na_2CrO_4	$\text{Cr}_2\text{O}_3\text{Fe}_2\text{O}_3$
	Ferricyanide	$\text{Na}_2\text{Fe}(\text{CN})_6$	$\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$
Copper	Chromate	Na_2CrO_4	$\text{CuO}, \text{Cr}_2\text{O}_3$
	Phosphate	Na_3PO_4	$\text{CuO}, \text{CuHPO}_4$
	Ferrous Sulfate	FeSO_4	FeOOH
Aluminum	Silicate	Na_2SiO_3	$\text{Al}_2(\text{SiO}_3)_3$
	Phosphate	Na_2HPO_4	AlPO_4
Zinc	Chromate	Na_2CrO_4	ZnCrO_4
	Phosphate	Na_2HPO_4	ZnHPO_4

TABLE V
Neutralizing Inhibitors

<u>Application</u>	<u>Inhibitor</u>	<u>Characteristic</u>
Boiler Water	Ammonia	Volatile
	Morpholine	Volatile
	Cyclohexylamine	Volatile
Sour Water	Polyamines	
Crude Oil Production	Alkyl Amines	
	Fatty Amines	
Petroleum Refining	Na ₂ CO ₃	Non-Volatile
	NH ₃	Volatile
	NaOH	Strong Base
Ethylene Glycol Coolant	Na ₂ B ₄ O ₇ ·10H ₂ O	Buffer

TABLE VI
Classification System for Inhibitors

<u>Description</u>	<u>Examples</u>
1. Barrier Layer Formers	
1.1 Adsorbed Layer Formers	Acetylenic Alcohol in HCl
1.1.1 Cathodic Inhibitors	
1.1.2 Anodic Inhibitors	
1.1.3 Mixed Reactors	
1.2 Oxidizing Inhibitors - Passivators	NaNO ₂ in Water
1.3 Conversion Layer Formers	
1.3.1 Insoluble Corrosion Products	Phosphate
1.3.2 Cathodic Deposits	CaCO ₃
2. Neutralizing Inhibitors	
2.1 Volatile Neutralizers	Cyclohexylamine in Boilers
2.2 Non-Volatile	Amines in Brine
3. Scavengers	
3.1 Oxygen Scavengers	Na ₂ SO ₃ in Boilers
3.2 Decomposition Inhibitors	Dioxane in CH ₃ CCl ₃
4. Miscellaneous	
4.1 Biological Growth Inhibitors	Quaternary Amines
4.2 Scale Inhibitors	Phosphonate
4.3 Other	H ₂ O in NH ₃

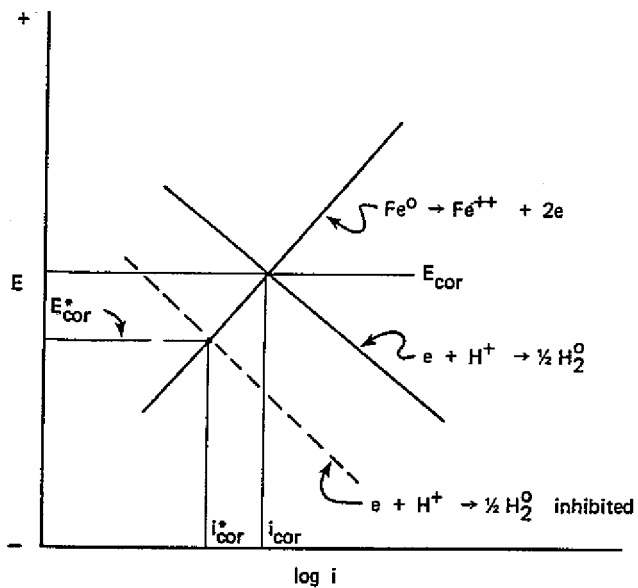


Figure 1 - Schematic Polarization Diagram Illustrating Cathodic Inhibitor in an Acid Solution. Note the Negative Corrosion Potential Shift.

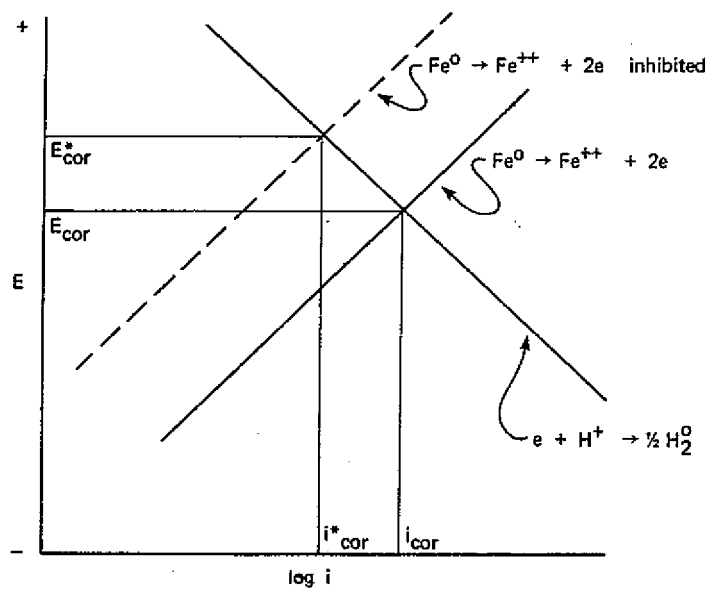


Figure 2 - Schematic Polarization Diagram Illustrating Anodic Inhibitor in an Acid Solution. Note the Positive Corrosion Potential Shift.

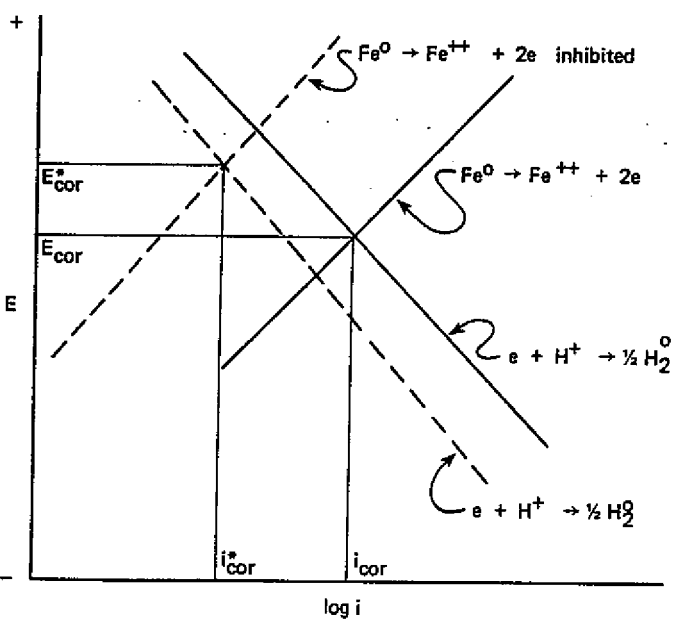


Figure 3 - Schematic Polarization Diagram Illustrating a Mixed Inhibitor in an Acid Solution. Note the Minimal Potential Shift Relative to the Degree of Inhibition.

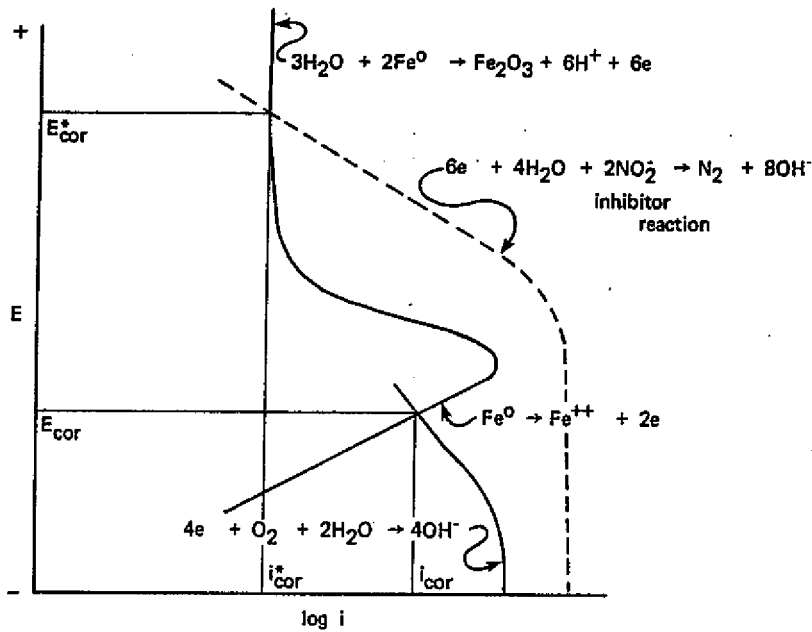


Figure 4 - Schematic Polarization Diagram for Nitrite Inhibition of Steel - A Passivating Inhibitor.

FALEX PIN & VEE BLOCK TESTS OF ORGANOAMMONIUM TUNGSTATE AND MOLYBDATE AND SODIUM TUNGSTATE IN OIL AND WATER

[illegible]